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DEC 15 1967

NATIONAL BUREAU OF STANDARDS REPORT

9647

PERFORMANCE OF CONVERSION COATINGS ON MAGNESIUM ALLOYS
IN MARINE AND SALT SPRAY (FOG) ENVIRONMENTS

By

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Engineering Metallurgy Section

To

Materials Division
Naval Air Systems Command
Department of the Navy
Project No. RRMA 2001



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Performance of Conversion Coatings On Magnesium Alloys
In Marine and Salt Spray (Fog) Environments

- References: (a) National Bureau of Standards Report No. 5261,
"Performance of HAE and Dow 17 Anodic Coatings on
Magnesium Alloys In Marine and Salt Fog Environments,"
dated April 26, 1957.
- (b) Naval Air Systems Command (BUaer) letter Aer-AE-432/128,
dated 27 July 1954.

Introduction: Poor performance by HAE and Dow 17 anodic conversion coatings on sand cast magnesium alloy AZ91C in tidewater and in salt spray environments was reported in Reference (a). In that investigation it was found that the rate of corrosive attack was greater on specimens coated by the Dow 17 process than on similar specimens coated by the HAE process. Specimens were attacked more rapidly on one end than on the other. There were indications that the poor performance may have been due to inhomogeneities and impurities in the cast specimens.

Since the initiation of the above tests, improvements have been reported for both the HAE and Dow 17 anodic coatings. These include variations in thicknesses obtainable and in post (sealing) treatments. In addition other types of anodic conversion coatings have been developed. As a result of the past experience and of recent developments, Reference (b) requested that additional tests be conducted to evaluate the protection given by conversion coatings, both painted and unpainted, on wrought AZ31A-H24 and sand cast AZ91C-T6 magnesium alloys in the salt spray and in marine environments. Because of the results reported in Reference (a), it was stipulated that additional tests for sand cast AZ91C be conducted on material with controlled amounts of iron, nickel and copper.

Materials: The following conversion coatings were investigated:

<u>Chemical Conversion</u> <u>Coatings</u>	<u>Anodic Conversion</u> <u>Coatings</u>
Dow 7	HAE
Dow 19 (brush-on)	SOK
	CR-22
	Dow 17

The alloys used in this investigation were wrought magnesium alloy AZ31A-H24 and sand cast magnesium alloy AZ91C-T6 (controlled purity). All materials were furnished by the Magnesium Division, Dow Chemical Company, Midland, Michigan. The chemical composition of the alloys as furnished by the Dow Chemical Company is as follows:

Element	Alloy	
	<u>AZ31A-H24</u>	<u>AZ91C-T6</u> ⁽¹⁾
	<u>Percent by Weight</u>	
Aluminum	2.8	9.04
Calcium	0.032	< 0.01
Copper	0.010	0.003
Iron	0.016	0.0032
Iron	-	0.004 ⁽²⁾
Manganese	0.43	0.47
Nickel	< 0.0005	< 0.001
Lead	< 0.001	< 0.001
Silicon	< 0.001	0.012
Tin	< 0.01	< 0.01
Zinc	1.04	0.57
Beryllium	0.0003	-

(1) Metal for all panels was melted down in a 2000 lb pot and poured from two 600 lb ladles. Values given are the average obtained from analyses of both ladles.

(2) Wet chemical analysis, other analyses are spectroscopic.

The wrought AZ31A-H24 alloy material submitted was in the form of panels with dimensions of 0.064 in. x 4 in. x 9 in. and 0.064 in. x 4 x 14 in. The sand cast AZ91C-T6 alloy submitted was in the form of individual cast panels, 0.375 in. x 3 in. x 8 in.

Specimen Preparation - General: The initial preparation of panel surfaces prior to coating was performed by the Metallurgical Laboratories of the Magnesium Division of the Dow Chemical Company, Midland, Michigan. The sand cast AZ91C-T6 alloy panels were sandblasted and acid pickled. The wrought AZ31A-H24 alloy panels were pickled in an acetic-nitrate solution (standard production pickle).

After the initial surface preparation by the Dow Chemical Company, the panels were submitted to NBS for codifications for identification purposes and distribution to the various coating processors. Coatings were applied by the following processors.

<u>Coating</u>	<u>Processor</u>
Dow 7	Brooks and Perkins, Detroit, Michigan.
Dow 17	Dow Chemical Company, Metallurgical Laboratory, Midland, Michigan.
HAE and CR-22	Frankford Arsenal, Pitman-Dunn Laboratories, Philadelphia, Pennsylvania
SOK	National Bureau of Standards Electrodeposition Section Washington, D. C.
Dow 19 (brush-on)	National Bureau of Standards Washington, D. C.

Details concerning the application of the various coatings are given in Table 1.

Specimen Preparation-Intentional Damage: In order to determine the corrosion protection given by the repair of damaged coatings, one specimen of each alloy from each coating group was intentionally damaged by scribing with a pointed instrument, several areas on each, deep enough to penetrate the coating to the base metal. Dow 19 conversion coating was then applied to these areas on each specimen with a brush. Dow 19 (brush-on) coating was also applied to one surface of one of the uncoated wrought AZ31A-H24 alloy specimens and to one surface on each of two of the uncoated sand cast AZ91C-T6 magnesium alloy samples.

Specimen Preparation - Painting: Paint coatings were applied by NBS to some of the specimens from each of the coating groups. The following paint systems were used on both sand cast AZ91C-T6 and wrought AZ31A-H24 magnesium alloy specimens:

Paint Systems

- (1) Wash primer, Specification MIL-C-8514, One coat.
- (2) Zinc chromate primer, Specification MIL-P-7962, Two coats.
- (3) Acrylic-nitrocellulose lacquer - Two coats.
 - (a) Top surfaces, light gull gray camouflage
Specification MIL-L-19538.
 - (b) Bottom surfaces, gloss white, Specification MIL-L-19537.

Exposure - General: For exposure, specimens were divided into four lots as follows: (1) controls, (2) salt spray tests, (3) marine atmosphere tests and (4) tidewater tests. A listing of painted and unpainted specimens exposed in each of the three test environments is given in Tables 2 and 3. The control specimens were stored at NBS in desiccated cabinets.

Exposure - Salt Spray: Three separate salt spray exposure tests were conducted on coated specimens of each alloy at the National Bureau of Standards. Specimens were subjected to the mist formed by atomizing a 20% NaCl solution maintained at $95^{\circ}\text{F} + 2^{\circ}$, -3° in a standard salt-fog chamber. The specimens were inclined 15° from the vertical.

Exposure - Marine Atmosphere: Marine atmosphere exposure tests were conducted in the 80 foot lot at the Kure Beach, N. C. test site of the International Nickel Company, Inc. The specimens were inclined in the test racks at an angle of 30° from the horizontal and faced towards the ocean. Exposure periods are given in Tables 2 and 3.

Exposure - Tidewater: Tidewater exposure tests were conducted in sea water at the Harbor Island, N. C. test site of the International Nickel Company. Specimens were exposed vertically and were totally immersed in the sea water at high tide and totally exposed to the atmosphere at low tide. Exposure periods for specimens from each alloy and coating groups are given in Tables 2 and 3.

Results - Painted and Unpainted Specimens: Corrosion products were removed from the unpainted exposed specimens by immersing them in a 20% chromic acid solution. The immersion time employed was dependent upon the concentration of corrosion products present on any particular specimen. The paint coatings were stripped by immersing the exposed painted specimens in acetone to remove the lacquer and then into a proprietary agent to remove the primer coatings. Subsequent to the above procedures the panels were examined visually for estimations of the corrosion damage. The results obtained on examinations of unpainted and painted specimens are given in Table 2 for the wrought AZ31A-H24 magnesium alloy and in Table 3 for the sand cast AZ91C-T6 magnesium alloy.

Results - Salt Spray (Fog) Tests: The results obtained from 3 separate salt spray (fog) tests are given in Tables 2 and 3. Figures 1 and 2 show the typical attack on representative specimens after 1000 hours exposure. The thick HAE coating with the post treatment was judged to be the best for the wrought AZ31A-H24 magnesium alloy while the thick Dow 17 coating with the post treatment was judged best for the sand cast AZ91C-T6 magnesium alloy.

Deterioration of all of the coatings on either alloy was characterized by localized failures of the coating followed by subsequent pitting of the base metal. This is shown in figure 1 for the wrought AZ31A-H24 magnesium alloy and in figure 2 for the sand cast AZ91C-T6 magnesium alloy. The declining order of the coatings, arranged according to the protection given is in Table 4.

Paint failures were noted on wrought AZ31A-H24 magnesium alloy specimens that had been given the Dow 7 and the thick SOK surface treatments. Similar paint failures were also noted on the sand cast AZ91C-T6 magnesium alloy specimens that had been surface treated with thick Dow 17 (post treated and not post treated). These failures occurred one on each of two of the three separate tests conducted.

Results - Marine Atmosphere Tests: Results obtained from visual examination of the sand cast AZ91C-T6 specimens exposed for 24 months in the marine atmosphere revealed no apparent deterioration regardless of surface treatment. Similar specimens, after 110 months exposure, still retained what appeared to be the rough cast surfaces, however the coatings had visibly deteriorated on all specimens except that on the specimen with the CR-22 surface treatment. This specimen still retained a portion of the green coating on approximately one-third of the surface. The general appearance of these specimens as a whole is best described as gray to grayish-white with no apparent deterioration of the metallic surfaces.

Of the surface treated wrought AZ31A-H24 magnesium alloy specimens exposed for 24 months in the marine atmosphere, the one with the thick HAE coating plus post treatment was judged to be the best. For those specimens that had been exposed 110 months, the surfaces that had been treated with the thick HAE coating and the post treatment were still judged to be the best. The coatings had completely deteriorated and the specimens were coated with a film of pale yellow corrosion products.

Deterioration of the wrought magnesium alloy specimens was initiated by localized failure of the coated surfaces which subsequently resulted in pitting of the base metal at these failed areas. Corrosion pits observed on all of the coated specimens were generally shallow in depth.

Paint failures were observed on most of the painted wrought AZ31A-H24 magnesium alloy panels after 24 months exposure in the marine atmosphere. There were no paint failures on panels with the following coatings: thick Dow 17 (post treated and not post treated), thick HAE (post treated) and CR-22. Paint failures were more prevalent on the specimens with the thin HAE coating. Generally the adhesion of the paint coatings was exceptionally good on all surface treated sand cast AZ91C-T6 magnesium alloy specimens except on those with the thin SOK coating. After 110 months

exposure in the marine atmosphere, the paint coatings on all of the specimens appeared to have sustained deterioration from erosion of the painted surfaces. There were paint failures along the bottom edge of all of the surface treated wrought AZ31A-H24 magnesium alloy specimens; however, the CR-22 surface treated specimen was the only one with no paint failures at other areas. There were no paint failures on the sand cast AZ91C-T6 magnesium alloy specimens that had been given the CR-22 or the thick SOK coating except at areas along the bottom edge of the specimens. Paint coating failures on all of the other sand cast specimens were of a local nature and few in number (less than 10); however, the paint coating that was applied to the specimens with the thin and thick Dow 17 surface treatments had eroded to the primer coating over approximately one-fifth of the surface of the specimen.

Results - Tidewater Exposure Tests: The results obtained from visual examination of the surface treated wrought AZ31A-H24 and sand cast AZ91C-T6 magnesium alloys after varying exposure periods in tidewater are given in Tables 2 and 3, respectively.

These results indicate that the thick HAE coating with the post treatment provides the greatest protection for the wrought AZ31A-H24 alloy. Localized coating failures and subsequent pitting of the base metal varying in degree were observed on all of the surface treated specimens after 34 days exposure; however, perforation of the base material had not occurred until after an exposure period in excess of 90 days. Examination of specimens exposed for 166 days revealed that the pitting corrosion had perforated all of the specimens. The severity of attack and the number of perforations varied with the surface treatment given the specimens. The attack on representative specimens after 166 days exposure in the tidewater is shown in figure 3. The least corroded areas are located at the top of the specimens. These areas were the first to emerge and the last to submerge during tidal changes. Accordingly this area would most likely dry quicker and remain dry longer than the other areas and would therefore not have as high a corrosion rate. While the specimen having the thick HAE coating and post treatment had been perforated at local areas, it may be seen that a major portion of the surface had not been attacked.

The thick HAE coating plus post treatment and the CR-22 coating provided the greatest protection for sand cast AZ91C-T6 magnesium alloy specimens. The thin HAE surface treatment also gave good protection to the sand cast alloy but to a slightly lesser degree. Corrosion damage on specimens of this alloy was not of sufficient intensity to cause penetration of the specimens. However, attack on all specimens was more severe along one edge and at areas adjacent to this edge than at other areas on the specimens. Figure 4 shows representative specimens of each coating type after 203 days immersion in the tidewater racks.

Visual examination of the specimens whose coatings had been scored and then repaired with the Dow 19 (brush-on) coating revealed that after 34 days tidal immersion there was some attack within the scored areas. This attack was noted on all of the wrought AZ31A-H24 magnesium alloy specimens and on the sand cast AZ91C-T6 magnesium alloy specimens with the thick HAE coating (post treated and not post treated).

The paint coatings on the Dow 7, the thin HAE and the thin and thick SOK surface treated specimens were the least protective for the wrought AZ31A-H24 magnesium alloy. Failures were observed on specimens exposed for 203 days in tidewater. Similarly, failures of the paint coatings on the thin Dow 17 coating were observed after 455 days of tidal immersion. The paint coating on the thick HAE coating gave good protection after 240 days immersion in tidewater, except at areas where marine fouling was observed. There were no failures after 455 days of tidal immersion on wrought magnesium alloy specimens with the thick Dow 17 coating (post treated and not post treated), the thick HAE coating (post treated) or the CR-22 coating.

Failures of the paint coatings applied over the Dow 7, thick Dow 17 (post treated and not post treated) and the thin HAE coatings were noted on the sand cast AZ91C-T6 magnesium alloy specimens after 204 days of tidal immersion.

Summary: Salt spray (fog) tests and marine environmental tests were conducted on painted and unpainted surface treated wrought AZ31A-H24 and sand cast AZ91C-T6 (controlled purity) magnesium alloys. The surface treatments investigated were: Dow 7, Dow 17, Dow 19, HAE, CR-22 and SOK conversion coatings. Variations in these treatments included thin and thick coatings for the Dow 17, HAE and SOK coatings. In addition post treatments (or sealing treatments) were given to the thick coated Dow 17 and the thick coated HAE specimens. The Dow 19 (brush-on) coating was applied to one surface of specimens of both alloys that had been pickled only and to surface treated areas on specimens of both alloys where the coating had been intentionally damaged. Specimens given the Dow 19 treatment were exposed in tidewater only.

The salt spray tests were conducted for a period of 1,000 hours. Exposures in tidewater ranged from 34 days to 455 days for the wrought AZ31A-H24 alloy and 34 days to 204 days for the sand cast AZ91C-T6 alloy. The marine atmosphere exposures were for periods of 24 months and 110 months.

The results obtained show:

- (1) The thick HAE coating with the post treatment gave the most protection to the wrought AZ31A-H24 magnesium alloy in all three environments.
- (2) The thick Dow 17 coating (post treated) gave the most protection to the sand cast AZ91C-T6 magnesium alloy in the salt spray tests.
- (3) The CR-22 coating adhered to the sand cast AZ91C-T6 alloy for the longest time in the marine atmosphere. Moreover, there were no visible indications of corrosive attack on any of the specimens of this alloy after 110 months exposure regardless of the surface treatment employed.
- (4) The thick HAE coating (post treated) and the CR-22 coating gave the most protection to the sand cast AZ91C-T6 alloy in tidewater.
- (5) The declining merit of the coatings, arranged according to the protection given specimens in salt spray tests, was as follows:

Wrought AZ31A-H24 magnesium alloy

Thick HAE (post treated)
CR-22
Thick SOK
Thick Dow 17 (post treated)
Thin SOK
Thick Dow 17
Thin HAE
Thin Dow 17
Thick HAE
Dow 7

Sand cast AZ91C-T6 magnesium alloy

Thick Dow 17 (post treated)
Thin HAE
Thick HAE (post treated)
CR-22
Thin SOK
Thick Dow 17
Dow 7
Thick SOK
Thick HAE
Thin Dow 17

- (6) The declining order of the coatings, arranged according to the protection given specimens in tidewater, was as follows:

Wrought AZ31A-H24 magnesium alloy

Thick HAE (post treated)
CR-22
Thick SOK
Dow 7
Thin SOK
Thin HAE
Thick HAE
Thin Dow 17
Thick Dow 17
Thick Dow 17 (post treated)

Sand cast AZ91C-T6 magnesium alloy

Thick HAE (post treated)
CR-22
Thin HAE
Thick Dow 17 (post treated)
Dow 7
Thin SOK
Thin Dow 17
Thick Dow 17
Thick SOK
Thick HAE

- (7) The declining order of the coatings, arranged according to the protection given specimens in the marine atmosphere, was as follows:

Wrought AZ31A-H24 magnesium alloy

Thick HAE (post treated)
Thick Dow 17 (post treated)
Thick Dow 17
Dow 7
Thick SOK
Thin HAE
Thin SOK
Thin Dow 17
CR-22
Thick HAE

- (8) Visual examination of the surface treated AZ91C-T6 magnesium alloy after 110 months exposure in the marine atmosphere did not reveal any indications of corrosive attack on the base metal. With the exception of the CR-22 coating, no visible trace of any of the coatings was noted after 36 months exposure. No traces of the Dow 7 and the thick SOK coatings were visible after a one year exposure. The declining order of merit for these coatings, based on coating longevity, was as follows:

- CR-22
- Thick Dow 17 (post treated)
- Thick Dow 17
- Thick HAE (post treated)
- Thick HAE
- Thin HAE
- Thin Dow 17
- Thin SOK
- Thick SOK
- Dow 7

- (9) In one of the three salt spray tests performed, paint failures occurred on one of the sand cast AZ91C-T6 alloy specimens given the thick Dow 17 coating and in another test paint failures were noted on a specimen given the thick Dow 17 (post treated) coating. On wrought AZ31A-H24 alloy specimens paint failures were noted on all of the Dow 7 coated panels in all three tests performed and on two (one each from two of the three tests) thick SOK coated panels.
- (10) After 24 months in the marine atmosphere, paint failures were noted on all of the surface treated wrought AZ31A-H24 alloy specimens except those given the thick Dow 17 (post treated), the thick HAE (post treated) and the CR-22 coatings. After the same exposure period, the sand cast AZ91C-T6 alloy specimens with the paint over-lay on the thin SOK coating had scattered areas of paint failures.
- (11) The declining order of coatings with paint over-lays, arranged according to the protection given wrought AZ31A-H24 alloy specimens in tidewater, was as follows:

1. Thick Dow 17 (post treated and not post treated)
Thick HAE (post treated)
CR-22
2. Thin Dow 17

3. Thick HAE (failed at fouled areas).

4. Dow 7
Thin HAE
Thin SOK
Thick SOK

The paint over-lays on the Dow 7, the thick Dow 17 (post treated and not post treated) and the thin HAE coatings gave the least protection to the sand cast AZ91C-T6 magnesium alloy.

Table 1. Details of the various surface treatments given wrought magnesium alloy AZ31A-H24 and sand cast magnesium alloy AZ91C-T6. All specimens were given the pickle treatment prior to application of a surface treatment. Pickle solution used was dependent upon the alloy, as noted below.

<u>Surface Treatment</u>	<u>Process Details</u>
1. Bare pickled surface	<p>A. AZ31A-H24 -- Acetic-Nitrate pickle solution at 70 - 80° F. Glacial Acetic Acid - 25 1/2 fl. oz. Sodium Nitrate - 6 2/3 oz. Water to make 1 gallon.</p> <p>B. AZ91C-T6 -- Chromic-Nitric - HF pickle solution. Chromic acid - 37 1/2 oz. Nitric acid (70%) - 3 1/4 fl. oz. Hydrofluoric acid (60%) - 1 fl. oz. Water to make 1 gallon.</p>
2. Dow 7	<p>A. Panels were immersed for one minute (approx.) in a hydrofluoric acid (60% HF) solution, 20 fl. oz./gallon of water, rinsed in cold water.</p> <p>B. Immersed for 30 minutes in a boiling solution of; Sodium dichromate - 20 oz. Calcium fluoride - 1/3 oz. Water to make 1 gallon; rinsed in cold, then hot water and dried.</p>
3. Dow 17	<p>Bath composition: Ammonium acid fluoride - 40 oz. Sodium dichromate - 13.3 oz. Phosphoric acid (85%) - 11.5 fl. oz. Water to make 1 gallon. Temperature for operation - 180° F. Voltage - DC</p> <p>A. Thin coating (a) AZ31A-H24 - 75 volts at 20 amp/sq ft, for 2 1/2 minutes. (b) AZ91C-T6 - 73 volts at 20 amp/sq ft, for 3 1/2 minutes</p> <p>B. Thick coating (a) AZ31A-H24 - 94 volts at 20 amp/sq ft, for 15 minutes (b) AZ91C-T6 - 90 volts at 20 amp/sq ft, for 21 minutes.</p> <p>C. Post Treatment on Dow 17, thick coating. Immersed for 15 minutes in a 5% solution of sodium tetrasilicate (water glass) maintained at 200 - 212° F.</p>

Table 1. (Continued)

Surface TreatmentProcess Details

4. HAE

Bath composition:

	oz/gal
Potassium hydroxide	20.0
Aluminum hydroxide	4.5
Trisodium phosphate	4.5
Anhydrous potassium fluoride	4.5
Potassium manganate	2.5

A. Thin coating (AZ31A-H24 and AZ91C-T6).

1. Hot alkaline cleaner.
2. Cold water rinse.
3. Chromic acid, 20%, solution at room temperature for 2 minutes.
4. Cold water rinse.
5. Processed in HAE solution (above), 55 to 60° C, 18 minutes, 7 volts DC at 40 amp/sq ft.
6. Cold water rinse.
7. Dip in 0.2% solution of sodium dichromate at 80 - 90° C for 2 minutes, no rinsing, air dried.

B. Thick coating.

1. AZ31A-H24.
 - (a) Hot alkaline cleaner.
 - (b) Cold water rinse.
 - (c) Processed in HAE solution (above), room temperature, voltage 0 - 58, 15 amp/sq ft for 8 minutes.
 - (d) Cold water rinse.
 - (e) Dip in bifluoride-dichromate solution, 1 minute, air dried. No rinsing after dip in bifluoride-dichromate solution.
 - (1) Solution -
 - Ammonium bifluoride - 13 oz/gal.
 - Sodium dichromate - 2.5 oz/gal.
 - (f) Aged in humid atmosphere at 175° F and 83% relative humidity for 3 hours.

2. AZ91C-T6

The same treatment as described under 1, except that the panels were dipped in a 20% chromic acid solution at room temperature for 3 minutes and rinsed in cold water between (b) and (c).

Table 1. (Continued)

Surface Treatment

Process Details

- C. Thick coating plus post treatment.
AZ31A-H24 and AZ91C-T6.
1. Hot alkaline cleaner.
 2. Cold water rinse.
 3. Processed in HAE solution (above), room temperature, voltage 0 - 80, 15 amp/sq ft, for 75 minutes.
 4. Cold water rinse.
 5. Dip in bifluoride-chromate solution for 1 minute and air dried without rinsing.
 6. Aged in humid atmosphere at 175° F and 83% relative humidity for 3 hours.
 7. Another 1 minute dip in the bifluoride-dichromate solution and air dried without rinsing.
 8. Aged at 175° F and 83% relative humidity for 4 hours.

CR-22

AZ31A-H24 and AZ91C-T6

- A. Hot alkaline cleaner.
 - B. Cold water rinse.
 - C. Dip in acid pickle (90 parts water, 8 parts nitric acid (conc.) and 2 parts sulfuric acid (conc.)).
 - D. Cold water rinse.
 - E. Dip in 20% chromic acid solution.
 - F. Cold water rinse.
 - G. Processed in CR-22 bath, 90° C, voltage 0 - 320, 15 amp/sq ft, 12 minutes.
- Bath composition:

Hydrofluoric acid (52%)	- 25 ml/l.
Phosphoric acid (85%)	- 50 ml/l.
Chromic trioxide	- 25 g/l.
Ammonium hydroxide	- 160 ml/l.

SOK (Alkaline-chromate)

- A. Bath composition:
 - Sodium hydroxide - 0.75 molar
 - Sodium dichromate - 0.75 molar
- B. Temperature 70° C
- C. Current - AC at 120 amp/sq ft.
- D. Cleaner
 - (1) Hot alkaline cleaner
 - (2) AZ31A-H24 - solution containing 250 g. chromic acid and 20 g. calcium nitrate per liter.
 - (3) AZ91C-T6 - solution containing 37.5 oz. chromic acid, 3.25 fl. oz. nitric acid (conc.) and 1 fl. oz. hydrofluoric acid (60%) per gallon.

Table 1. (Continued)

Surface Treatment

Process Details

Thin coating:

Specimens were anodized in A for
10 minutes, rinsed in hot water
and air dried.

Thick coating:

Specimens were anodized in A for
30 minutes, rinsed in hot water
and air dried.

Table 2. Results of visual examination of wrought magnesium alloy AZ31A-H24 after exposure periods in various environments.

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks (y)
Dow 7	3	1000			M	
	3	1000			M	
	3	1000			M	
	2		34		D	
	2		90		H	
	8		166		M	
	3			727	D	
	3			3290 (z)	G	
	3	1000			M	
	3	1000			M	
Dow 17, thin	3	1000			M	
	3	1000			M	
	3	1000			M	
	2		34		G	
	2		90		H	
	8		166		M(5)	x(3), a(1), c(4)
	3			727	E	
	3			3290 (z)	G	
	3	1000			L	
	3	1000			L	
Dow 17, thick	3	1000			L	
	3	1000			L	
	3	1000			L	
	2		34		G	
	2		90		H	
	8		166		M(3)	x(5), a(2), b(1)
	3			727	D	
	3			3290 (z)	G	

Table 2. (Continued)

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks (y)
Dow 17, thick + post treatment	3	1000			K	
	3	1000			K	
	3	1000			K	
	2		34		I	
	2		90		I	
	8		166		M(4)	x(4), a(1), b(1), e(2)
	3			727	D	
	3			3290 (z)	G	
HAE, thin	3	1000			L	
	3	1000			L	
	3	1000			L	
	2		34		H	
	2		90		I	
	8		166		M(7)	x(1), c(4), d(1)
	3			727	D	
	3			3290 (z)	G	
HAE, thick	3	1000			M	
	3	1000			M	
	3	1000			M	
	2		34		F	
	2		90		I	
	8		166		M	c(3)
	3			727	G	
	3			3290 (z)	G	

Table 2. (Continued)

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks (y)
HAE, thick + post treatment	3	1000			F(2), K(1)	
	3	1000			K	
	3	1000			K	
	2		34		B	
	2		90		B	
	2		166		M	
	5		203		M	
	1		271		M	
	3			727	B	
	3			3290 (z)	B	
	3	1000			K	
	3	1000			K	
SOK, thin	3	1000			K	
	2		34		G	
	2		90		I	
	8		166		M(7)	x(1), c(6)
	3				E	
	3			727	G	
				3290 (z)		
	3	1000			K	
	3	1000			K	
	3	1000			K	
	2		34		E	
	2		90		H	
	8		166		M(7)	x(1)
	3			727	E	
	3			3290 (z)	G	

Table 2. (Continued)

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks (y)
SOK, thick	3	1000			L	
	3	1000			L	
	3	1000			L	
	2		34		F	
	2		90		I	
	8		166		M	
	3			727	D	
	3			3290 (z)	G	
Bare, pickled surface	3	1000			M	
	3	1000			M	
	3	1000			M	
	2		34		H	
	2		90		I	
	8		166		M(5)	x(3), b(1), c(2), d(1)
	3			727	D	
	3			3290 (z)	G	
Dow 7, painted	3	1000			BB	
	3	1000			BB	
	3	1000			BB	
	3		203		EE	
	2		240		EE	
	1		455		FF	
	3			728	CC	
	3			3290 (z)	EE	

Table 2. (Continued)

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks (y)
Dow 17, thin, painted	3	1000			AA	
	3	1000			AA	
	3	1000			AA	
	3		203		AA	
	3		455		CC	
	3			728	BB	
	3			3290 (z)	CC+HH	
	3					
Dow 17, thick, painted	3	1000			AA	
	3	1000			AA	
	3	1000			AA	
	3		203		AA	
	3		455		AA(2)	x(1)
	3			728	AA	
	3			3290 (z)	CC+HH	
	3					
Dow 17, thick + post treatment, painted	3	1000			AA	
	3	1000			AA	
	3	1000			AA	
	3		203		AA	
	2		240		GG	
	1		455		AA	
	3			728	AA	
	3			3290 (z)	CC+HH	
HAE, thin, painted	3	1000			AA	
	3	1000			AA	
	3	1000			AA	
	3		203		EE	
	3		240		FF	
	3			728	DD	
	3			3290 (z)	EE+HH	
	3					

Table 2. (Continued)

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks (y)
HAE, thick, painted	3	1000			AA	
	3	1000			AA	
	3	1000			AA	
	3		203		AA	
	3		240		CC(2)	x(1)
	3			728	BB	
	3			3290 (z)	CC+HH	
	3					
HAE, thick + post treatment, painted	3	1000			AA	
	3	1000			AA	
	3	1000			AA	
	3		203		AA	
	3		455		AA	
	3			728	AA	
	3			3290 (z)	BB+HH	
	3					
CR-22, painted	3	1000			AA	
	3	1000			AA	
	3	1000			AA	
	3		203		AA	
	3		455		AA	
	3			728	AA	
	3			3290 (z)	HH	
	3					
SOK, thin, painted	3	1000			AA	
	3	1000			AA	
	3	1000			AA	
	3		203		CC(2), GG(1)	
	3		240		CC(2), GG(1)	
	3			728	BB(2), CC(1)	
	3			3290 (z)	EE+HH	
	3					

Table 2. (Continued)

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks (y)
SOK, thick, painted	3	1000			AA	
	3	1000			AA(2), CC(1)	
	3	1000			AA(2), BB(1)	
	3		203		CC	
	2		240		CC	
	1		455		CC	
	3			728	BB(2), CC(1)	
	3			3290 (z)	EE+HH	
x	-	Specimens lost from racks.				
y	-	Numbers in parenthesis are number of specimens reported. When no number is given, number of specimens reported is number of specimens exposed.				
z	-	Specimens still on exposure for long term data.				
B	-	Few shallow corrosion pits.				
D	-	Scattered shallow corrosion pits.				
E	-	Scattered medium deep corrosion pits.				
F	-	Scattered deep corrosion pits.				
G	-	General shallow corrosion pits.				
H	-	General medium deep corrosion pits.				
I	-	General deep corrosion pits.				
K	-	Specimens perforated, few small holes.				
L	-	Specimens perforated, some holes.				
M	-	Specimens perforated, numerous holes.				
a	-	1/2 of specimen remaining.				
b	-	2/3 of specimen remaining.				
c	-	7/8 of specimen remaining.				
d	-	4/5 of specimen remaining.				
e	-	1/3 of specimen remaining.				

Table 2. (Continued)

AA	-	No paint failures.
BB	-	Scattered pin point paint failures.
CC	-	1 to 10 small areas of paint failure.
DD	-	Scattered areas of paint failure.
EE	-	Scattered areas of paint failure and few areas of surface attack.
FF	-	Same as EE plus corrosion products, pitting and some general attack.
GG	-	Scattered areas of paint failure where marine fouling had occurred.
HH	-	General erosion of the painted surface.

Table 3. Results of visual examination of sand cast magnesium alloy AZ91C-T6 after exposure periods in various environments.

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks
Dow 7	1	1000			E	
	1	1000			E	
	1	1000			E	
	2		34		A	
	1		89		D	
	1		203		E	
	1			728	A	
	1			3290 (z)	*	Gray appearance
Dow 17, thin	1	1000			E	
	1	1000			E	
	1	1000			E	
	2		34		B	
	1		89		G	
	1		203		H	
	1			728	A	
	1			3290 (z)	*	Gray to wash white appearance
Dow 17, thick	1	1000			E	
	1	1000			E	
	1	1000			E	
	2		34		A	
	1		89		E	
	1		203		H	
	1			728	A	
	1			3290 (z)	*	Gray to wash white appearance

Table 3. (Continued)

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks
Dow 17, thick + post treatment	1	1000			D	
	1	1000			D	
	1	1000			D	
	2		34		A	
	1		89		E	
	1		203		E	
	1			728	A	
	1			3290 (z)	*	Grayish-white appearance
HAE, thin	1	1000			E	
	1	1000			D	
	1	1000			E	
	2		34		B	
	1		89		D	
	1		203		E	
	1			728	A	
	1			3290 (z)	*	Grayish-white appearance
HAE, thick	1	1000			E	
	1	1000			E	
	1	1000			E	
	2		34		B	
	1		89		D	
	1		203		H	
	1			728	A	
	1			3290 (z)	*	Grayish-white appearance

Table 3. (Continued)

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks
HAE, thick + post treatment	1	1000			B	
	1	1000			B	
	1	1000			C	
	2		34		A	
	1		89		D	
	1		203		E	
	1			728	A	
	1			3290 (z)	*	Gray
CR-22	1	1000			C	
	1	1000			C	
	1	1000			C	
	2		34		A	
	1		89		A	
	1		203		D	
	1			728	A	
	1			3290 (z)	*	Gray with approx. one third of coating remaining
SOK, thin	1	1000			E	
	1	1000			E	
	1	1000			E	
	2		34		A	
	1		89		E	
	1		203		E	
	1			728	A	
	1			3290 (z)	*	Grayish-white appearance

Table 3. (Continued)

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks
SOK, thick	1	1000			D	
	1	1000			D	
	1	1000			E	
	2		34		A	
	1		89		E	
	1		203		E	
	1			728	A	
	1			3290 (z)	*	Light gray appearance
Bare, pickled surface	2	1000			H	
	2	1000			H	
	2	1000			H	
	4		34		D	
	2		89		E	
	2		203		H	
	2			728	A	
	2			3290 (z)	*	Grayish white
Dow 7, painted	1	1000			AA	
	1	1000			AA	
	1	1000			AA	
	1		90		AA	
	1		204		CC	
	1			728	AA	
	1			3290 (z)	CC+HH	
	1					
Dow 17, thin, painted	1	1000			AA	
	1	1000			AA	
	1	1000			AA	
	1		90		AA	
	1		204		AA	
	1			728	AA	
	1			3290 (z)	CC+HH	
	1					

Table 3. (Continued)

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks
Dow 17, thick, painted	1	1000			AA	
	1	1000			AA	
	1	1000			BB	
	1		90		AA	
	1		204		CC	
	1			728	AA	
	1			3290 (z)	CC+HH	
	1					
Dow 17, thick + post treatment, painted	1	1000			BB	
	1	1000			AA	
	1	1000			AA	
	1		90		AA	
	1		204		BB	
	1			728	AA	
	1			3290 (z)	CC+HH	
	1					
HAE, thin, painted	1	1000			AA	
	1	1000			AA	
	1	1000			AA	
	1		90		AA	
	1		204		EE	
	1			728	AA	
	1			3290 (z)	DD+HH	
	1					
HAE, thick, painted	1	1000			AA	
	1	1000			AA	
	1	1000			AA	
	1		90		AA	
	1		204		AA	
	1			728	AA	
	1			3290 (z)	CC+HH	
	1					

Table 3. (Continued)

Surface Treatment	Number of Specimens Exposed	Salt Spray, Hours	Tidewater, Days	Marine Atmosphere, Days	Visual Rating (y)	Remarks
HAE, thick + post treatment, painted	1	1000			AA	
	1	1000			AA	
	1	1000			AA	
	1		90		AA	
	1		204		AA	
	1			728	AA	
	1			3290 (z)	CC+HH	
CR-22, painted	1	1000			AA	
	1	1000			AA	
	1	1000			AA	
	1		90		AA	
	1		204		AA	
	1			728	AA	
	1			3290 (z)	HH	
S0K, thin, painted	1	1000			AA	
	1	1000			AA	
	1	1000			AA	
	1		90		AA	
	1		204		AA	
	1			728	DD	
	1			3290 (z)	DD+HH	
S0K, thick, painted	1	1000			AA	
	1	1000			AA	
	1	1000			AA	
	1		90		AA	
	1		204		AA	
	1			728	AA	
	1			3290 (z)	HH	

Table 3. (Continued)

*	-	No discernible pitting corrosion on the surfaces.
y	-	Numbers in parenthesis are number of specimens reported. Where no number is given, number of specimens reported is number of specimens exposed.
z	-	Specimens still on exposure for long term data.
A	-	No corrosion.
B	-	Few shallow corrosion pits.
C	-	Few deep corrosion pits.
D	-	Scattered shallow corrosion pits.
E	-	Scattered corrosion pitting of medium depth.
H	-	General corrosion pitting of medium depth.
AA	-	No paint failures.
BB	-	Scattered pin point paint failures.
CC	-	1 to 10 small areas of paint failure and corrosion pitting.
DD	-	Scattered areas of paint failure.
EE	-	Scattered areas of paint failure and few areas of surface attack.
HH	-	General erosion of the painted surface.

Table 4. Declining order of conversion coatings arranged according to the protection given wrought AZ31A-H24 and sand cast AZ91C-T6 magnesium alloys in salt spray, marine atmosphere and tide-water environments.

<u>Salt Spray</u>	<u>Marine Atmosphere</u>	<u>Tidewater</u>
<u>Wrought AZ31A-H24 Magnesium Alloy</u>		
HAE, thick + post treatment CR-22	HAE, thick + post treatment Dow 17, thick + post treatment	HAE, thick + post treatment CR-22
SOK, thick Dow 17, thick + post treatment	Dow 17, thick Dow 7	SOK, thick Dow 7
SOK, thin Dow 17, thick HAE, thin Dow 17, thin HAE, thick Dow 7	SOK, thick HAE, thin SOK, thin Dow 17, thin CR-22 ^(a) HAE, thick	SOK, thin HAE, thin HAE, thick Dow 17, thin Dow 17, thick Dow 17, thick + post treatment
<u>Sand-cast AZ91C-T6 Magnesium Alloy^(b)</u>		
Dow 17, thick + post treatment HAE, thin	CR-22 Dow 17, thick + post treatment	HAE, thick + post treatment CR-22
HAE, thick + post treatment CR-22	Dow 17, thick HAE, thick + post treatment	HAE, thin Dow 17, thick + post treatment
SOK, thin Dow 17, thick Dow 7 SOK, thick HAE, thick Dow 17, thin	HAE, thick HAE, thin Dow 17, thin SOK, thin SOK, thick Dow 7	Dow 7 SOK, thin Dow 17, thin Dow 17, thick SOK, thick HAE, thick

(a) Most of the green coating maintained after 110 months exposure; however, specimen pitted at failed areas. Pits were larger in diameter than on other specimens with coatings ranked above.

(b) Listing of the coatings on specimens exposed in the marine atmosphere is based on durability. Corrosion protection given by the coatings on this alloy was not readily determinable in that even after 110 months exposure there were no visible indications of corrosive attack.

THE UNIVERSITY OF CHICAGO

DEPARTMENT OF CHEMISTRY

PHYSICAL CHEMISTRY

LECTURE NOTES

BY

PROFESSOR

JOHN

DOUGLAS

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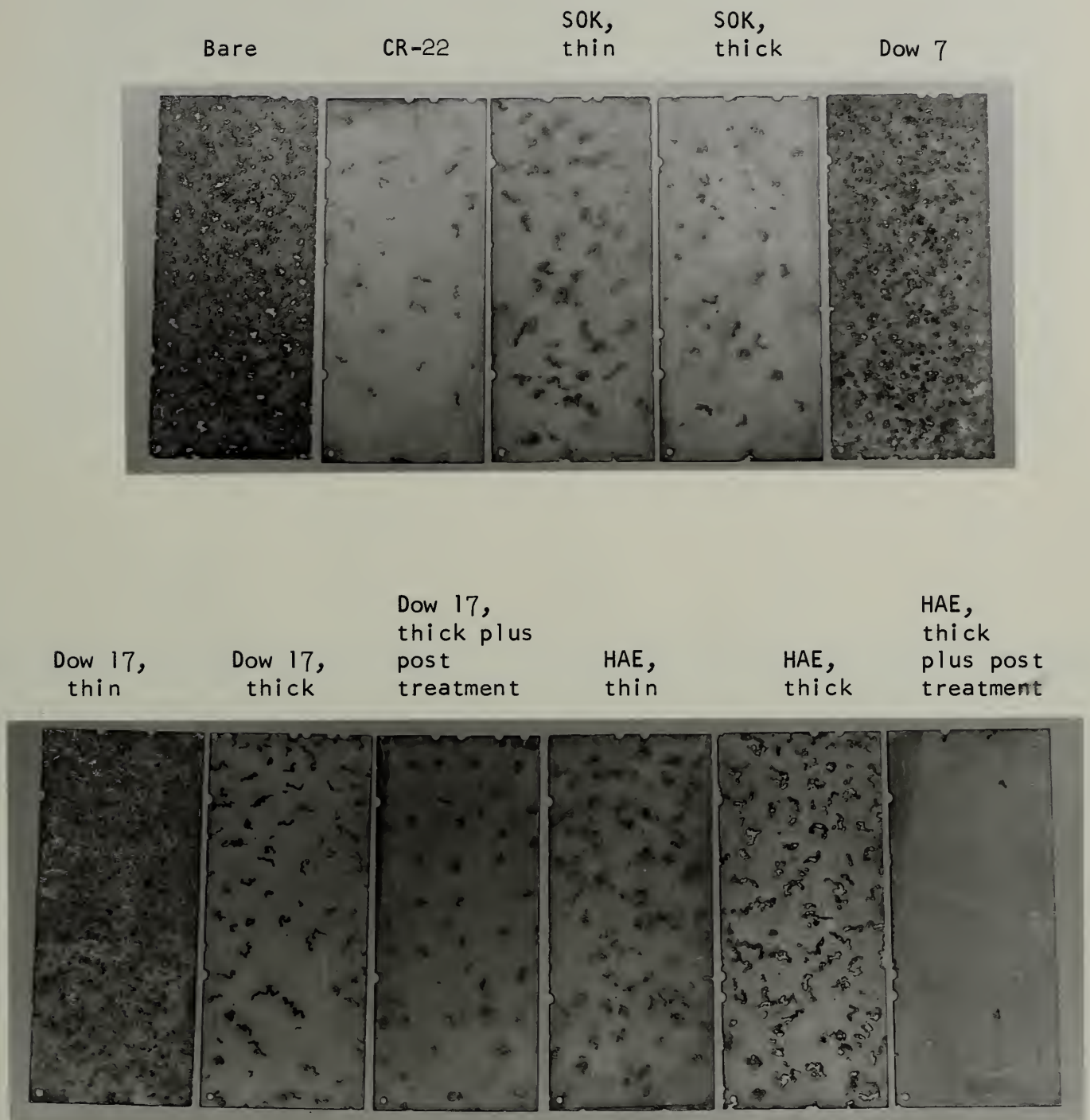


Figure 1. Appearance of representative surface treated wrought AZ31A-H24 magnesium alloy specimens after 1000 hours exposure in salt spray and after cleaning to remove corrosion products and conversion coatings. X 1/4.

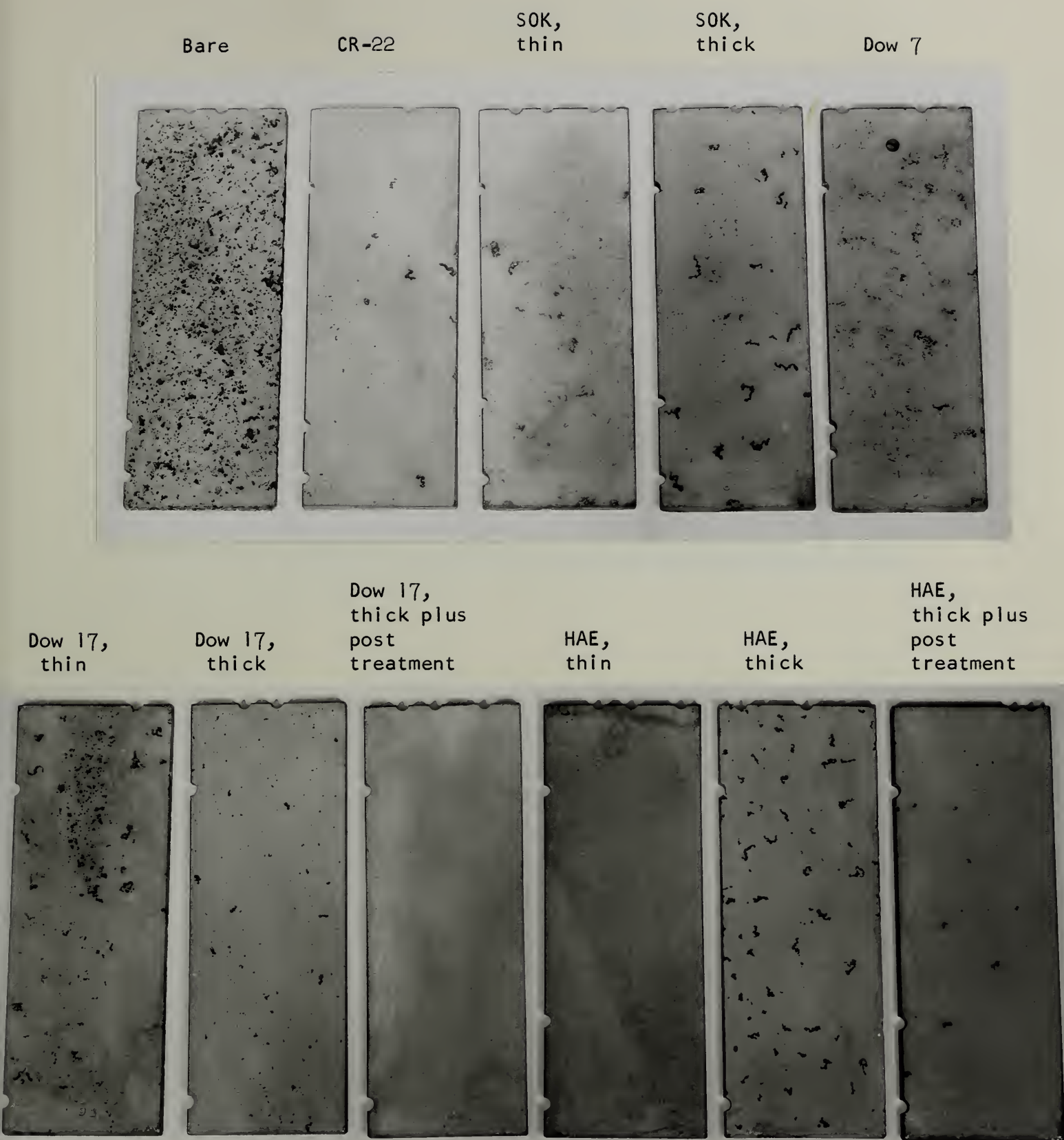


Figure 2. Representative surface treated sand cast AZ91C-T6 magnesium alloy specimens after 1000 hours exposure in the salt spray and after cleaning to remove corrosion products and conversion coatings. X 1/3.

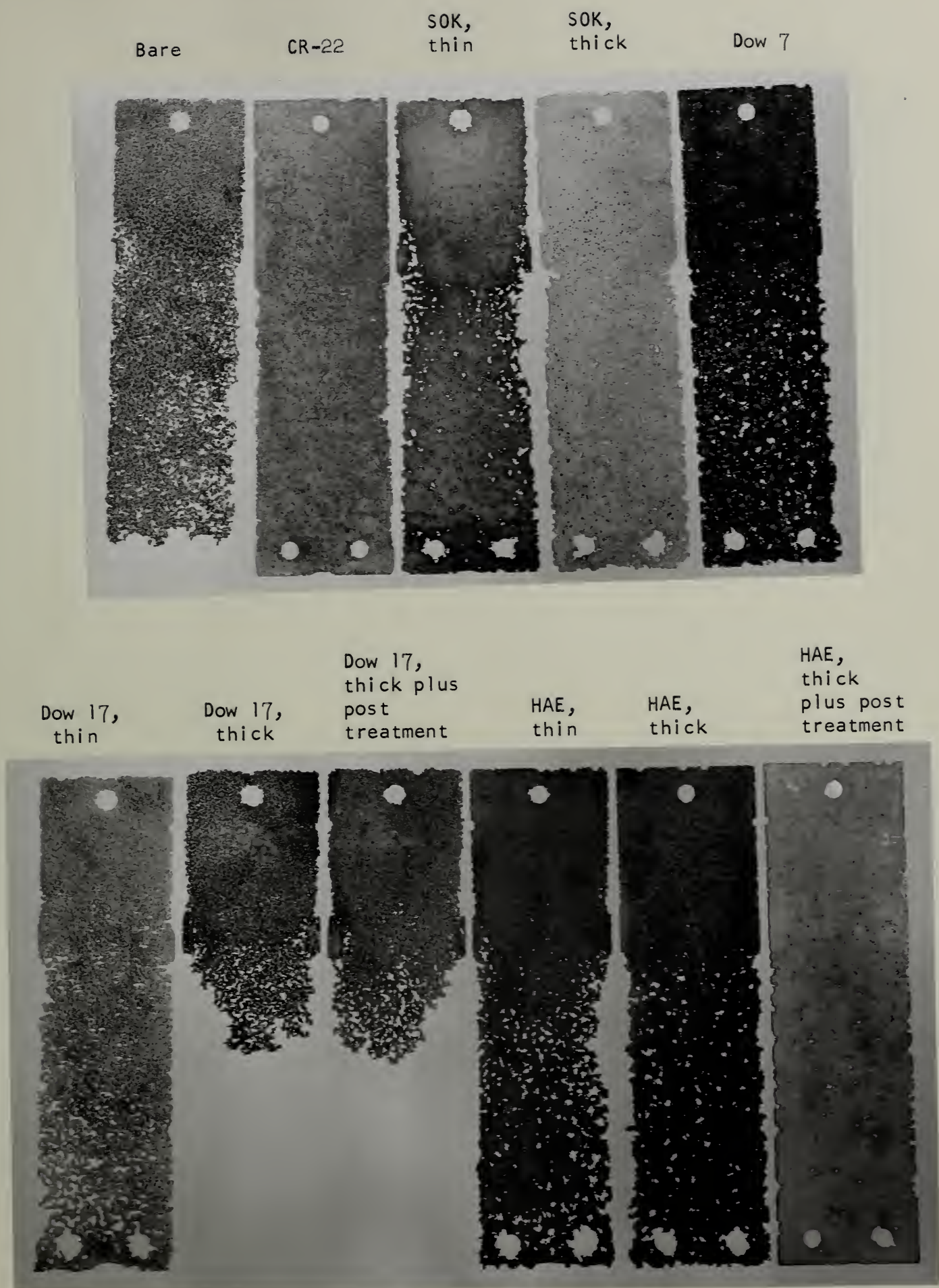


Figure 3. Effect of 166 days exposure in the tidewater on surface treated wrought AZ31A-H24 magnesium alloy specimens. Specimens are shown after removal of corrosion products and conversion coatings. X 1/4.

Bare

CR-22

SOK,
thinSOK,
thick

Dow 7

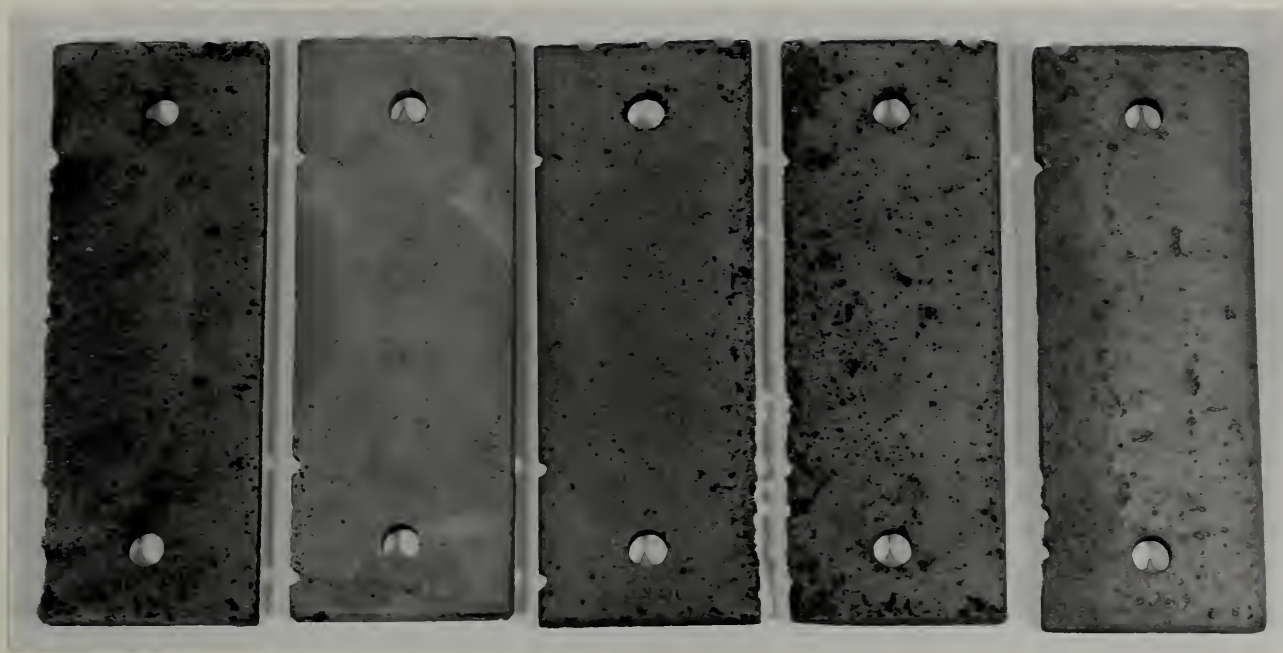
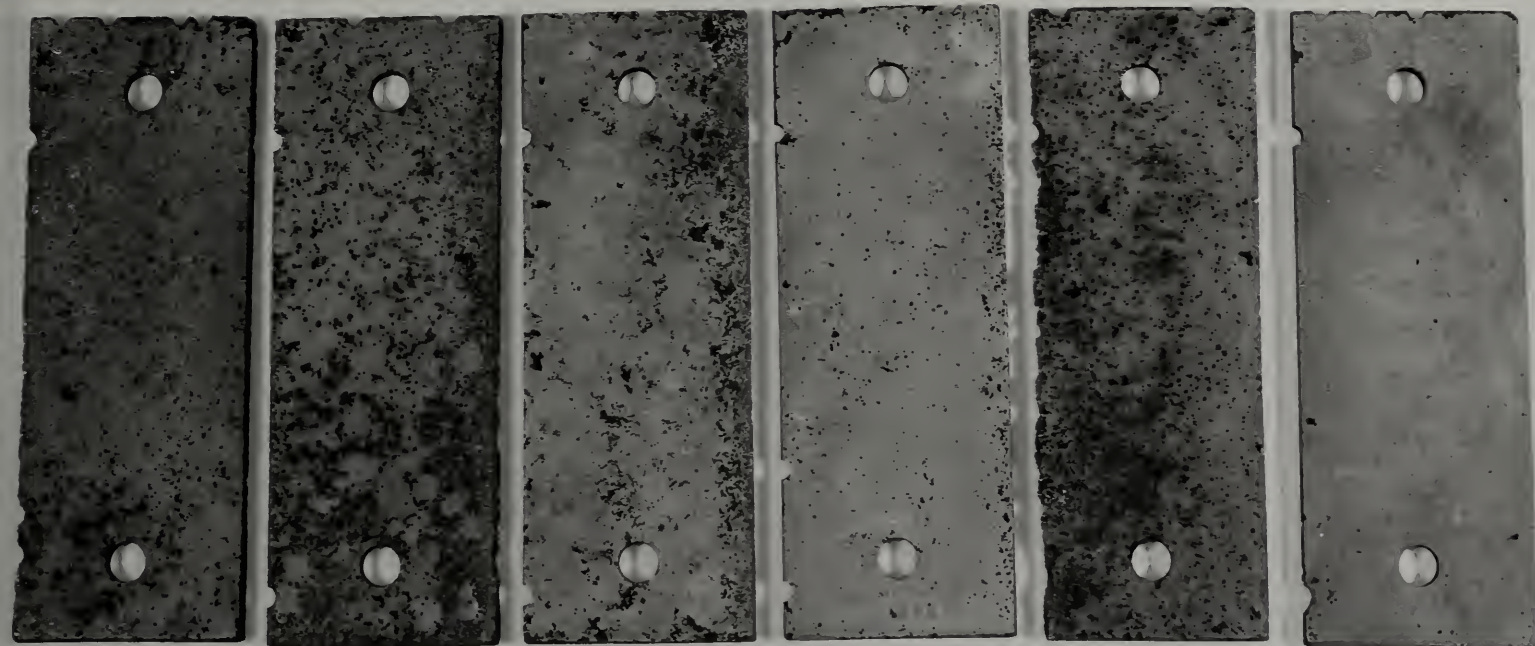
Dow 17,
thinDow 17,
thickDow 17,
thick plus
post
treatmentHAE,
thinHAE,
thickHAE,
thick,
plus post
treatment

Figure 4. Effect of 203 days exposure in the tidewater on surface treated sand cast AZ91C-T6 magnesium alloy specimens. Specimens are shown after removal of corrosion products and conversion coatings. X 1/3.

